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For many years it has been known that magnesic oxalate is carried down with calcic oxalate in the ordinary course of quantitative analysis. This is only one case of the very general phenomenon of concomitant precipitation, or occlusion, sometimes explained with the help of van't Hoff's conception of "solid solution,"* and not widely understood, no matter what name may be used. It is of considerable interest, both practically and theoretically, to obtain evidence concerning the mechanism of this class of analytical irregularities.

In a foregoing paper,† one of us has shown that occlusion is probably the distribution of an *undissociated* substance between the solution and the nascent solid. If this is the case, the amount of material occluded should be directly proportional to the concentration of the undissociated part of the substance in question. The application of this idea to the present case of calcium and magnesium seemed capable of furnishing a further clue to the theory of the general problem, as well as of providing a more satisfactory analytical method in this particular case. Since the magnesium comes down with the calcium in the form of oxalate, it is the concentration of the *undissociated magnesium oxalate* in the solution which will determine the amount of the occlusion, if this hypothesis be true. According to the law of mass action and the dissociation hypothesis, this concentration may be increased by adding either constituent ion in excess. It may be diminished by adding a large excess of any other partially ionized substance,‡ especially those

* Schneider, Z. phys. Chem. **10**, 425 (1892).

† Richards, These Proceedings, **35**, 377 (1900).

‡ Compare Arrhenius, Z. phys. Chem. **31**, 198 (1899).

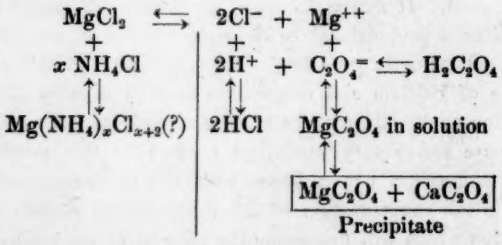
which form a complex ion or undissociated substance in solution involving either magnesium or oxalic acid.

One of the most effective causes diminishing the concentration of the magnesic oxalate, and therefore the occlusion, should be the hydrogen ion, for this tends to remove the oxalic ion, and hence to cause the ionization of undissociated magnesic oxalate.

Another effective cause should be an increase in the concentration of ammonic salts present, which not only exert the effect of any other partially dissociated salts, but have also the well-known property of forming complex compounds with magnesium. This formation naturally removes magnesic ions and hence magnesic oxalate from the solution.

A third obvious means of diminishing the concentration of the magnesic oxalate is by diluting the solution. By this process, the actual amount of undissociated oxalate is diminished, and the concentration of the undissociated part is thus diminished even more rapidly than in the ratio of the changing volumes. All of these tendencies except the second apply to the calcium as well as to the magnesium, although to a less extent, for calcic oxalate is far less soluble than magnesic oxalate. Calcium has not so great a tendency to form complexes with ammonic salts as magnesium.

These relations are partially expressed by the following scheme, in which no attempt is made to express the exact nature or the ionization of the magnes-ammonium complex: —



Reviewing the older work upon this subject, one finds that most of the known facts support the hypothesis. Fresenius, in the few experiments which are recorded in the end of the second volume of his "Quantitative Analysis," * showed that the weight of the calcic precipitate obtained was less when the dilution was greater; that it was

* Fresenius, Quantitative Analyse, 2, 821 (1877–1887).

diminished by the presence of an excess of either ammonic hydrate or ammonic chloride. When acetic acid was present, too little precipitate was obtained, and a very large excess of oxalate in alkaline solutions gave too much precipitate. But Fresenius attacked the problem merely in an empirical fashion; the guiding hypothesis of the present day had not yet been suggested. It did not occur to him to study the effect of gradual precipitation in a strongly acid solution.

Most writers of handbooks upon quantitative analysis have accepted Fresenius's method of double precipitation, and the recent literature upon the subject is unusually scanty. In a paper, of which we have seen only an abstract,* Hefelmann calls attention to the necessity of using dilute solutions in order to attain satisfactory results; but other important references to the subject in periodical literature could not be found. A good method devised by H. P. Talbot, not to be found in the periodicals, will be mentioned later.

For our experiments calcic chloride and magnesic chloride or sulphate were prepared separately in a state of great purity. By the repeated crystallization of the nitrate, the calcium material was freed from its usual impurities, and the carbonate was precipitated from this nitrate by means of pure ammonic carbonate. Standard solutions of this material in hydrochloric acid were made from time to time, and the concentration of these solutions was determined with the utmost care by precipitation with ammonic oxalate, according to the method to be described. Magnesic chloride and sulphate were carefully purified by repeated crystallization, and experimental proof was obtained of the absence of calcium from them. The magnesium solutions were always of a strength approximately equivalent to the calcium. Ammonic chloride was made by passing pure ammonia gas into freshly made hydrochloric acid; oxalic acid was especially purified; and all the ammonia used was freshly prepared in platinum vessels.

In the first place, the worst possible results were obtained in order to show how great an improvement was possible by the successive introduction of the modifications suggested above. To neutral solutions of a mixture of 25 c.c. each of the magnesium and calcium solutions, made up to 200 c.c., was added an excess of ammonic oxalate, but without the addition of either ammonic chloride or acid. The two precipitates thus formed were ignited at a very high temperature until constant in weight. Below are recorded the results: —

* Zeitschr. anorg. Chem. **18**, 401 (1898).

PRECIPITATION IN ABSENCE OF PRECAUTION.

No. of Experiment.	Wt. of Ignited Precipitate.	Wt. of CaO taken (determined in Parallel Portions).	Difference. MgO present.	Error.
1	0.2743	0.2358	0.0385	+ 16.4%
2	0.2597	0.2358	0.0239	+ 10.1%
			Average error,	+ 13.3%

The next step was to test the effect of hydrochloric acid — or rather of the concentration of ionized hydrogen — upon the occlusion. Since in this case from an acid solution all of the calcium could not be precipitated, a larger amount was used, but the concentration of the magnesium was the same as before. 25 c.c. of the magnesium solution, 75 c.c. of the calcium solution, and 10 c.c. of normal hydrochloric acid were diluted up to 200 c.c. To this solution, heated to boiling, were added 27 c.c. of normal oxalic acid, to which had previously been added 10 c.c. of normal hydrochloric acid for the sake of diminishing its dissociation. Over half of the calcium was precipitated in the form of fine white crystals of the oxalate. It is well known that the substances most capable of easy supersaturation are those which form the largest crystals; and conditions which tend to promote the solubility of a precipitate in general tend to promote its ease of supersaturation. Hence precipitates formed from solutions in which they are somewhat soluble, are more crystalline than those formed from liquids in which they are insoluble. Calcic oxalate is no exception to this general rule. The easily handled precipitate was collected, thoroughly washed, ignited to constant weight at a bright yellow heat, dissolved, reprecipitated, reignited, and weighed again. The results below show how comparatively small was the occlusion of magnesium in this precipitate.

PRECIPITATION FROM ACID SOLUTIONS.

No. of Experiment.	Weight of First Oxides.	Weight of CaO (2d).	MgO present.	Error.
3	0.4136	0.4100	0.0036	0.88%
4	0.4128	0.4087	0.0041	1.00%
			Average error,	0.94%

The average error attained only one-fourteenth of its previous magnitude. Thus the presence of acid has a remarkable restraining effect upon the occlusion; a fact in accordance with the prediction of the theory.

In the next place, the action of ammonic chloride was studied. A neutral solution of 25 c.c. each of the calcium and magnesium solutions was made up to 200 c.c. and treated with two grams of ammonic chloride and the same amount of ammonic oxalate as in the first experiment. Two trials of this process yielded the following results: —

THE EFFECT OF AMMONIC CHLORIDE.

No. of Experiment.	Weight of Oxides found.	Weight of CaO taken.	MgO present.	Apparent Error.
5	0.2376	0.2358	0.0018	0.77%
6	0.2364	0.2358	0.0006	0.25%
			Average error,	0.51%

About 1.1 milligrams more of calcic oxide was recovered from each of these solutions by the addition of much more ammonic oxalate. This precipitate, which fell after some time, was redissolved and reprecipitated before weighing in order to free it from magnesium. The total amount of magnesic oxide in the first precipitate was thus about one per cent, or somewhat more than in the precipitates from an acid solution.

These experiments show that ammonic chloride diminishes very much the tendency of the magnesic oxalate to be precipitated, but that it exerts also a similar although much less considerable effect upon the calcic oxalate. The more ammonic chloride is added, the greater concentration of oxalate ion is necessary completely to precipitate the calcium, but the more effective is the retention of the magnesium in the solution. The limit to the advisable amount of ammonic chloride depends upon the subsequent method to be used for the determination of the magnesium; but for ordinary purposes an equivalent-concentration ten times as great as that of the magnesium present should answer.

This action may be explained, as has already been stated, partly by an effect which would be caused by any electrolyte and partly by the additional formation of an unstable complex. The existence of this complex is abundantly confirmed by the other reactions of magnesium in the presence of a large amount of ammonic chloride. It is well known that many of the common reactions fail, and that other reactions, such

as the precipitation of ammonic magnesic phosphate, require more time for their completion, when much ammonic chloride is present.*

If, as a matter of fact, the occlusion is proportional to the concentration of the undissociated magnesic oxalate, additional ammonic oxalate, even in the presence of ammonic chloride, ought to increase the weight of the precipitate. The following experiments, similar to the last except that in each case three grams instead of one of ammonic oxalate were used, were made to test this point.

THE EFFECT OF EXCESS OF AMMONIC OXALATE.

No. of Experiment.	Weight of Oxides.	Weight of CaO taken.	MgO present.	Error.
7	0.2390	0.2358	0.0032	1.36%
8	0.2393	0.2358	0.0035	1.48%
			Average error,	1.42%

Thus a trebling of the amount of oxalate present increased the error by about a third of its previous value. At first one is surprised that the increase is not greater; but it must be remembered that the oxalate was added rather slowly, so that most of the precipitate was formed before a large excess of oxalate was present. It is chiefly the *concentration of the magnesic oxalate present at the instant of precipitation*, not the subsequent amount in contact with the precipitate, which influences the distribution. When the precipitate has once appeared as a solid, the action must be confined to the surface; for diffusion into solids is exceedingly slow because of their rigid structure.

A number of analyses were made in the hope of combining all the circumstances which tend toward complete separation, and of eliminating all those which oppose it; but yet further difficulties arose. It seemed probable that by *gradual* neutralization of an acid solution the calcic oxalate might be precipitated in an environment containing as little magnesic oxalate as possible, and thus be as free as possible from this impurity. The mode of procedure was as follows. To a mixture containing in 200 c.c., 25 c.c. each of the calcic and magnesic solutions, were added three grams of ammonic chloride, 1.6 grams of oxalic acid, and enough

* Compare Ostwald, Scientific Foundations of Analytical Chemistry (Macmillan, 1895), p. 136.

hydrochloric acid to keep the calcic oxalate in solution. Subsequently strong ammonia was poured very slowly into the liquid, with continual stirring, until the solution contained an excess of ammonia. Methyl orange was found to assist materially the exact neutralization.

PRECIPITATION BY CONCENTRATED AMMONIA.

No. of Experiment.	Weight of Mixed Oxides.	Weight of CaO taken.	Weight of MgO.	Error.
9	0.2373	0.2358	0.0015	0.6%
10	0.2383		0.0025	1.1%
11	0.2384		0.0026	1.1%
12	0.2387		0.0029	1.2%
			Average error,	1.0%

Some calcium was found in the mother liquors upon the addition of more ammonic oxalate; but this is included above. Evidently no material gain in accuracy is effected in this series, and the reason is not hard to find. The ammonia was so strong that it caused instant neutralization of the acid in its neighborhood; and hence the idea of the method was defeated, for the design was to effect a *gradual* neutralization, giving time for the supersaturated calcic oxalate to separate.

In the next series twice as much oxalic acid was used, but the ammonia added to effect the precipitation was far less concentrated.

PRECIPITATION BY DILUTE AMMONIA.

No. of Experiment.	Weight of Mixed Oxides.	Weight of CaO taken.	Weight of MgO.	Error.
13	0.2375	0.2358	0.0017	0.7%
14	0.2374		0.0016	0.7%
15	0.2369		0.0011	0.5%
16	0.2380		0.0022	0.9%
17	0.2379		0.0021	0.9%
			Average error,	0.74%

Thus, diluting the ammonia had the beneficial effect which was expected. In the presence of so much oxalate the solution was, of course, practically free from calcium, hence this result indicates a distinct improvement.

It has been already noticed that dilution of the original solution has been found by others to lessen the amount of magnesium carried down. This fact might have been easily predicted by the hypothesis that the phenomenon is regulated by the Distribution Law. It is further verified by two experiments given below, in which the method of Experiments 13–17 was repeated, except that the volume was 800 c.c. instead of 200 c.c.

THE EFFECT OF DILUTION.

No. of Experiment.	Weight of Mixed Oxides.	Weight of CaO taken.	Weight of MgO.	Error.
18	0.2369	0.2358	0.0011	0.42%
19	0.2371		0.0013	0.54%
			Average error,	0.48%

Here also no calcium could be recovered from the mother liquor, hence it is clear that the dilution was really of service, reducing the magnesic oxide from 0.74 per cent to 0.48 per cent. The theoretical diminution to less than a quarter of the former value was not to have been expected, for the addition of the ammonia in finite dilution introduces an irregularity for which it is impossible to make quantitative correction.

At this stage in the work it was found that a method of precipitation essentially identical with that just given had already been published by Professor H. P. Talbot in his admirable treatise on the elements of Quantitative Analysis.* So far as we know, no account of it is to be found elsewhere. Since no examples accompany this publication, the preceding work, which was wholly independent, affords useful confirmation of his method as an approximate one for rapid work.

The chief difference between the method of Talbot and ours lay in the respective amounts of oxalate, a much larger amount having been used in our work in order to insure the total precipitation of the calcium.

It is clear from the above account that this large initial excess of the

* Talbot, Quantitative Analysis (Macmillan), 3d ed. p. 42 (1899).

oxalate, although necessary so far as the calcium is concerned, must increase the amount of precipitated magnesium oxalate. But according to our original hypothesis, this excess is chiefly harmful when it is present at *the moment of precipitation*, although it is not really needed to prevent the solution of traces of calcic oxalate until the precipitation is practically finished. Hence the oxalic acid also should be added gradually, or at least in two portions, the first to supply enough oxalate to combine with the bulk of the calcium, and the second to diminish the solubility of the last traces. This plan was followed in the following work.

Another point was as yet undecided, — the length of time needed for the essentially complete separation of the calcium. Hence five determinations similar to the above were made with solutions each capable of yielding 0.1496 grams of lime and an equivalent quantity of magnesia. The only variation in these experiments was in the time elapsing between precipitation and filtration.

THE EFFECT OF THE TIME BETWEEN PRECIPITATION AND FILTRATION.

No. of Experiment.		Weight of Precipitate.	Error.
20	Filtered after standing ½ hour	0.1488	− 0.53%
21	" " " ¾ hour	0.1492	− 0.27%
22	" " " 24 hours	0.1501	+ 0.33%
23	" " " 48 hours	0.1507	+ 0.73%
24	" " " 80 hours	0.1511	+ 1.00%
	Amount of calcic oxide present,	0.1496	

The filtrates from the first two of these (Nos. 20 and 21) deposited traces of calcic oxalate on standing for two hours, but the others did not deposit a trace in several days. From these five experiments two conclusions may be drawn: first, that several hours are needed for a separation of the last weighable traces of calcium, even when much ammonic oxalate is used; and secondly, that after the calcium has all been precipitated, magnesium oxalate is absorbed by the precipitate at a fairly constant although very slow rate, from a solution which will of itself deposit no solid. The magnesic oxalate is slowly occluded by

the precipitate or deposited upon it even after the precipitation of the calcium salt.

This points to another flaw in the earlier work, — namely, the solutions, which had all been allowed to stand for at least sixteen hours before filtering, had been left too long in contact with their precipitates.

In a case of this kind great accuracy is to be obtained only by a succession of approximations; hence it seemed worth while again to make a series of precise analyses, embodying all the advantages which had been found up to this point, in order to discover from their possible variations if there might be still another cause of error as yet undetected.

Newly prepared very pure solutions were used in these analyses, which were made two years after the ones previously detailed. All the precautions suggested by the foregoing pages were heeded, and two series of results were obtained, one from calcium solutions only, and the other from solutions containing precisely the same amount of calcium with an equivalent amount of magnesium. These are given below in parallel columns: —

Precipitation of Pure Calcic Oxalate.
(Volume at precipitation = 200 c.c.)

No. of Analysis.	Time of Digestion.	Weight of CaO.
25	3.5 hours	0.3063
26	3.5 "	0.3064
27	3.5 "	0.3065
28	3.5 "	0.3064
	Average,	0.3064

Precipitation of Calcium in Presence of Magnesium.
(Volume at precipitation = 500 c.c.)

No. of Analysis.	Time of Digestion.	Weight of CaO.
29	2.5 hours	0.3060
30	2.5 "	0.3060
31	3.5 "	0.3064
32	3.5 "	0.3066
33	3.5 "	0.3058
Average of last three,		0.3063

The agreement between the two averages is very striking; it is to some extent due to a compensation of errors. Even when we have made due allowance for these, however, it furnishes strong evidence in favor of the hypothesis which led to the before mentioned precautions. Experiments 29 and 30, not included in the average, show that at the

end of two hours and a half there probably still remained a trace of calcium in the solution.

While the possibility of separating calcium from magnesium with considerable completeness by a single operation had thus been demonstrated, one point still remained to be studied. In the course of the washing of these precipitates of calcic oxalate, it was noticed that the wash-waters always gave a faint opalescence with neutral argentic nitrate, an opalescence which dissolved in nitric acid. Unlimited washing seemed not to free the precipitate from this substance, hence the substance must have been calcic oxalate itself. In short, calcic oxalate appeared to be soluble in boiling water to an extent sufficient to affect a precise analysis. Since no account of accurate determinations of the solubility of calcic oxalate in boiling water could be found, the next problem was to determine this solubility.

The calcic oxalate was precipitated in the usual manner and washed with exceeding thoroughness. A solution, not necessarily saturated, but closely resembling one which might be obtained in the process of washing, was made by stirring the powder for fifteen minutes with water in a platinum dish kept at the desired temperature. Of the three usual methods of analyzing such a solution, — by weighing, titration, and the measurement of electrical conductivity, — volumetric determination

SOLUBILITY OF CALCIC OXALATE. SERIES I.

	Temperature = 90°.		
No. of Analysis.	Volume of Permanganate required by 100 c.c. of Sol.	Weight of Calcic Oxalate corresponding.	Remarks.
34	1.86 c.c.	0.00115	Fresh filter, thoroughly moistened.
35	1.81 c.c.	0.00112	Same filter as above.
36	1.81 c.c.	0.00112	Same filter as above.
	Temperature = 25°.		
37	1.10 c.c.	0.00068	Fresh filter.
38	1.06 c.c.	0.00066	Same filter as preceding.

seemed the best suited to the present purpose. The filtered solution was therefore titrated with a solution of approximately hundredth normal permanganate, of which one cubic centimeter corresponded to 0.00062 gram of calcic oxalate. The amount of the solution, 0.12 c.c., which was required to impart the usual pale pink color to the assay, was always subtracted from the total volume run out. In each analysis exactly a decilitre of calcic oxalate solution was used.

These results are typical of a number of similar determinations which were made in this way. The first portions running through a filter paper always seemed to contain slightly more calcic oxalate than the later portions, probably owing to the escape of fine particles which are retained by the filter when it has become somewhat clogged. The later values are probably the more reliable, hence it is clear that hot water will dissolve easily over a centigram per litre of calcic oxalate, while water at the ordinary temperature dissolves nearly seven milligrams per litre.

This solubility is altogether too great to be passed without heed in precise work. Its magnitude was such as to make desirable a more exact determination of a more nearly saturated solution.

The first problem to be solved in this connection was the retention of even the finest particles. The best filter papers of Schleicher and Schüll, Dreverhoff, and others were tested, all with the result already described; namely, that the first filtrate always yielded slightly more calcic oxalate than the following ones. Finally it was decided to use four layers of paper, and to reject at least half a litre of filtrate before beginning to collect for analysis. The filtration was effected by means of a platinum inverted filter devised by J. P. Cooke,* and a simple arrangement of tubes and stopcocks made the rejection of the first and the collection of the subsequent portions of filtrate an easy matter. The filtered liquid appeared perfectly clear on inspection in strong light. The inverted filter made it possible to maintain the filtering liquid at the desired temperature. The time of digestion at the higher temperatures was an hour; but at 25° an hour and a half was allowed. A very large platinum dish served as the vessel for digestion, and the liquid was suitably protected from the products of combustion of illuminating gas and other impurities. A diagram of the apparatus will furnish all further necessary explanation. As before, a hundred cubic centimeters of the solution served for each titration.

* These Proceedings, **12**, 124 (1876).

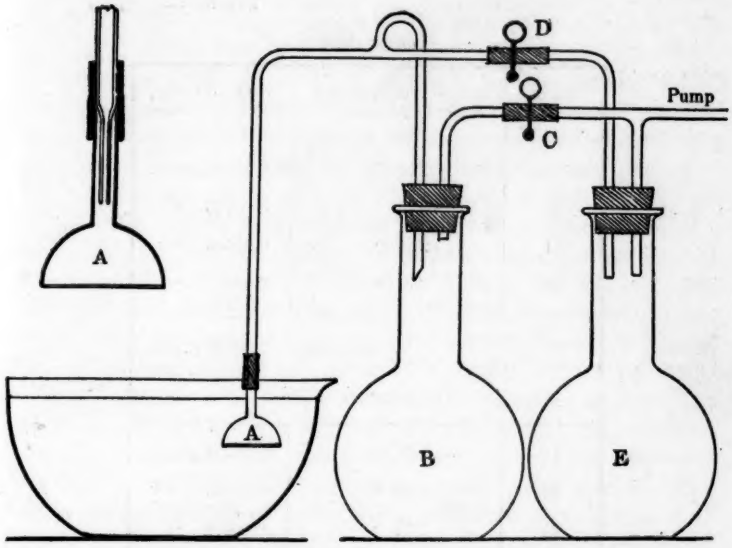


FIGURE I. APPARATUS FOR FILTERING.

A is the inverted filter, clad four-fold with filter paper. B is the collecting flask, which fills only when C is open and D closed. E serves to retain the rejected liquid.

It is not certain that these solutions were wholly saturated; but the difference in concentration between these and the earlier solutions, which had been digested during much less time, made it highly probable that any error from this cause would be less than the necessary errors of titration. Hence no further determinations were made.

After these determinations were finished, Kohlrausch and Rose's * determinations by means of electrical conductivity at lower temperatures were consulted, and were found to furnish agreeable confirmation of these independently obtained results. At 18° Kohlrausch and Rose's figure was 5.9 milligrams per litre, while our extrapolated value is 6.0 milligrams; and at 40° the respective figures are 8.0 and 8.4 milligrams. Our slightly larger values may be due to the fact that we determined all the calcic oxalate in solution, while Kohlrausch and Rose measured only that part which is dissociated. According to the table upon page 200

* Zeitschr. für phys. Chem., **12**, 234 (1890).

SOLUBILITY OF CALCIC OXALATE. SERIES II.

Temperature = 95°.

No. of Analysis.	Volume of Permanganate required by 100 c.c. Sol.	Weight of CaC_2O_4 in 100 c.c. Solution.
39	2.19 c.c.	0.00136 gram.
40	2.18 "	0.00135 "
41	2.35 "	0.00146 "
42	2.28 "	0.00141 "
		Average, 0.00140 gram.
	Temperature = 50°.	
43	1.55 c.c.	0.00096 gram.
44	1.56 "	0.00097 "
45	1.53 "	0.00095 "
46	1.52 "	0.00094 "
		Average, 0.000955 gram.
	Temperature = 25°.	
47	1.09 c.c.	0.00068 gram.
48	1.11 "	0.00069 "
49	1.08 "	0.00067 "
		Average, 0.00068 gram.

of Kohlrausch and Holborn's book (1898) this interpretation might account for the difference, but in any case they make no pretensions to great accuracy. In view of Ostwald's recent work on the surface tension of solids,* a more precise determination than ours would be of no service unless the diameters and shapes of the solid particles were defined.

* Ostwald's Zeitschr phys. Chem., **34**, 495 (1900).

In the light of all these facts, there can be no question that calcic oxalate is soluble enough to demand further precautions in washing than are usually taken. The obvious means of diminishing this solubility is to wash the precipitate with a dilute solution of ammonic oxalate, instead of with pure water. With the idea of testing the efficacy of this precaution, as well as with the purpose of determining the strength of a new solution of calcic chloride, the following series were made.

In the first place three portions, removed with a very exact 25 c.c. pipette, were individually precipitated by degrees in our usual fashion from a solution having a volume of two hundred cubic centimeters. They were each allowed to remain four hours before filtering. The weights of calcic oxide resulting upon ignition to constant weight at a bright yellow heat were respectively 0.3479, 0.3480, and 0.3480 gram. The last two of these were now dissolved in hydrochloric acid and reprecipitated with the utmost care by means of ammonic oxalate. The weights were now, after ignition, 0.3474 and 0.3475 gram respectively — an average loss of 0.00055 gram or 0.16 per cent. If pure water had been used for washing, the loss would have been much greater. This loss may have been due to incomplete precipitation, or to a slight solubility in the wash-water in spite of the presence of ammonic oxalate, or to the mechanical passage of exceedingly small particles through the filter. Whatever may be the cause, this deficiency is clearly a quantity which must apply to most if not all of the foregoing work. Its application does not cause sufficient change in the results to affect the conclusions which have been drawn ; in many cases of comparison each of the numbers compared is affected equally.

It became now an interesting question to carry out in the presence of magnesium the operations just described. Except for the degree of dilution, the other conditions were in every respect like those named. In two experiments where the precipitation took place in a volume of 300 c.c., the weights of impure calcic oxide were respectively 0.3491 and 0.3489 gram, a gain of a milligram, or 0.29 per cent. In two other cases where the volume was 600 c.c., the weights were 0.3486 and 0.3483 gram respectively, a gain of 0.13 per cent.

This last gain is almost exactly equal to the inevitable loss during filtration, so that the occluded magnesia almost exactly replaced the lime which is not collected.

The slightly impure specimens of lime of the last two experiments, weighing respectively 0.3486 and 0.3483 gram, were now dissolved and reprecipitated as oxalate, which was washed with ammonic oxalate as

before. The resulting specimens of oxide weighed respectively 0.3469 and 0.3474 gram, an average of 0.34715 gram, while the weights obtained by a similar double precipitation in the absence of magnesium averaged 0.34745 gram, or 0.3 milligram more. This difference is too small to have much significance, hence the conclusion is allowable that as much of the lime as is practicable had been precipitated.

It is clear from these experiments that the double precipitation usually practised, while certainly eliminating the magnesium, inevitably involves the loss of calcium. The single precipitation minimizes this last risk, and by the compensation of two errors very small in themselves, gives a result which is very near the truth.

The conclusions attained in this paper may be summarized as follows: —

1. All those conditions which tend to diminish the amount of undissociated magnesic oxalate in a solution tend to diminish the amount of this impurity in calcic oxalate precipitated from the solution.

2. Hence evidence is furnished supporting the hypothesis that occlusion is a distribution of an undissociated substance between the liquid and the "nascent" solid phase.

3. Magnesic oxalate is precipitated upon the calcic oxalate after this is deposited, although far more slowly than while it is being deposited. For this reason the filtration should not be too long delayed.

4. Calcic oxalate is sufficiently soluble in pure water to cause grave inaccuracies in precise quantitative work.

5. This solubility may be diminished, but not wholly prevented, by an excess of ammonic oxalate in the wash water.

6. By heeding all these relations, a reasonably precise separation of magnesium and calcium may be made in a single precipitation. The details are as follows: The magnesium in the solution should be not much stronger than fiftieth normal. About ten times the equivalent amount of ammonic chloride, and enough oxalic acid to combine with all the calcium, should be added to the mixed solution. It is well to diminish the dissociation of the oxalic acid beforehand by the addition of two or three times its equivalent amount of hydrochloric acid. To the boiling mixture, colored with a drop of methyl orange, should be added slowly a very dilute solution of ammonia, with continual stirring and occasional pauses. The final stages of neutralization should not be reached in less than half an hour.

When the neutralization has been effected, a very large excess of ammonic oxalate should be added, and the mixture should be allowed to

stand for four hours. The precipitated calcic oxalate should be thoroughly washed with water containing ammonic oxalate. The filtrate will contain all but about 0.1 or 0.2 per cent of the magnesium, and the precipitate will contain all but about the same proportion of the calcium.

7. The precipitate, having been formed slowly from a solution in which it was somewhat soluble, is distinctly crystalline and far more easily handled than if it had been suddenly precipitated. This is a general effect, which might render service in other cases.

CAMBRIDGE, MASS.
October, 1897, to February, 1901.